

# **AFRL-OSR-VA-TR-2013-0065**

Reversible Shape Memory Polymers and Composites: Synthesis, Modeling and Design

Patrick T. Mather, Ph.D., H. Jerry Qi, Ph.D., Martin Dunn, Ph.D.

Syracuse University March 2013 Final Report

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# REPORT DOCUMENTATION PAGE

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# Reversible Shape Memory Polymers and Composites: Synthesis, Modeling and Design

Final Report
February 1, 2009 through May 31, 2012

Grant No. FA9550-09-1-0195

Principal Investigator: Prof. Patrick T. Mather co-Principal Investigator: Prof. H. Jerry Qi co-Principal Investigator: Prof. Martin Dunn

Biomedical and Chemical Engineering Syracuse University Syracuse, NY 13244 315-443-8760

Program Manager: Dr. Les Lee AFOSR/NA

#### PROGRESS REPORT

Reversible Shape Memory Polymers and Composites: Synthesis, Modeling and Design (FA9550-09-1-0195)

Prof. Patrick T. Mather Syracuse University February 1, 2009 – May 31, 2012 Final Report

**3 January 2013** 

### I. OBJECTIVE

Reconfigurable multifunctional structures, which allow combined changes of shape, functionality and mechanical properties on demand, require new adaptive materials and novel chemistry that permit reversible modulation of mechanical properties in effective manner. They also demand the development of robust modeling and design tools based on a fundamental understanding of the complex and time-variant properties of the material and mechanization structure in diverse environments. In this research, we: 1) developed two new classes of two-way shape memory polymers (SMPs); 2) fostered these two SMPs to free-standing SMP composites with enhanced reversible modulation through novel composite design; 3) pursued a fundamental understanding of underlying physics of the proposed two-way SMPs and composites; 4) established modeling and simulation-design tools for applications of these novel materials for reconfigurable aerospace structures; and 5) exploreed design, fabrication and testing of novel SMP devices enabling for Air Force applications.

### II. APROACH

We have assembled a strong interdisciplinary team with strengths in materials chemistry and material science (Mather), composite mechanics and composite design (Dunn), polymer finite deformation constitutive modeling and numerical implementation (Qi). The expertise in our team is pivotal in successfully implementing the proposed work.

### III. SCIENTIFIC CHALLENGE

This collaboration between Syracuse University (PI Mather) and University of Colorado, Boulder (co-PI's Qi and Dunn) was quite aggressive, scientifically, presenting significant challenges in the elucidation of mechanisms involved in the newly discovered two-way shape (reversible) shape memory effect in polymers. Significant advances in experimental methods were required to attain the stated research goals.

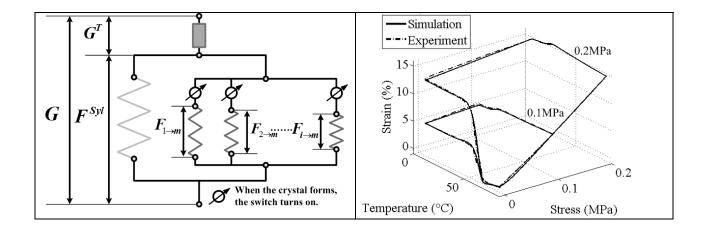
### IV. Technical Progress

This report is organized into progress made on several fronts: (i) Modeling and model-validation of Shape Memory Elastomeric Composites; (ii) Development of a Functionally Graded Shape Memory Polymer; and (iii) Development of a Shape Memory Assisted Self-Healing Polymer.

# IV(i) Modeling and Model Validation of Shape Memory Elastomeric Composites

Qi Ge, Xiaofan Luo, Erika D. Rodriguez, Xiao Zhang, Patrick T. Mather, Martin L. Dunn, H. Jerry Qi, "Thermo-mechanical Behaviors of Shape Memory Elastomer Composites," *Journal of Mechanics and Physics of Solids*, 60, 67-83 (2012).

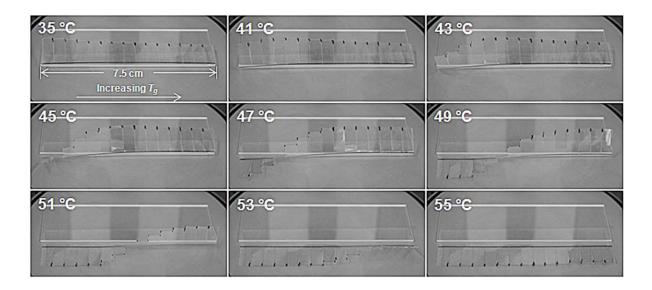
Shape memory polymers (SMPs) are polymers that can fix a temporary shape and recover their permanent shape in response to environmental stimuli such as heat, electricity, or irradiation. Most thermally activated SMPs use the macromolecular chain mobility change around the glass transition  $T_g$  to achieve the shape memory (SM) effects. During this process, the stiffness of the material typically goes through three orders of magnitude change. Recently, one of the PI's reported on a novel shape memory elastomeric composite (SMEC). This composite, composed of Sylgard and poly(ε-caprolactone) (PCL), is soft in both temporary and permanent shapes with moduli close to typical rubbers. In the SMEC system, Sylgard as an elastomeric matrix provides rubbery elasticity, while PCL, by using crystal-melt transition, serves as a reversible "switch phase" for shape fixing and recovery. The development of SMEC provides a paradigm for developing a wide array of smart polymer composites with different chemistries that utilize melt-crystal transition in polymers to achieve shape memory effect. It is therefore important to understand the thermomechanical behaviors and to develop corresponding material models. Further, a model is needed to allow rational design of SMEC-based mechanical devices. In this work, a 3D constitutive model was developed to describe the thermomechanical behaviors of SMEC. This model includes a kinetic description of non-isothermal crystallization and melting, which imparts SM capability of the SMEC system. The model assumes that the newly formed crystal phases are in the undeformed state, which tracks the kinematics of evolving phases. In order to improve the computational efficiency, the effective phase model (EPM) is adopted. The model accurately captures SM behaviors of the SMEC system exhibited in experiments. In the figures below, we show the model schematic (left) and the high quality of agreement between model and experiment for two different shape memory cycles, differing in their applied tensile stress.



IV(ii) Development of a Functionally Graded Shape Memory Polymer

A.M. DiOrio, X. Luo, K.-M. Lee, and P.T. Mather, "A Functionally Graded Shape Memory Polymer," *Soft Matter* **7** 68-74 (2011).

In this work, we developed methods and materials to prepare and characterize a functionally graded shape memory polymer (SMP) that, unlike conventional SMPs, has a range of transition temperatures that are spatially distributed in a gradient fashion within one single article. This was achieved by post-curing a pre-cured glassy SMP in a linear temperature gradient that imposes different vitrification temperature limits at different positions along the gradient. Utilizing indentation-based surface shape memory coupled with optical measurements of photoelastic response, the capability of this material to respond over a wide range of thermal triggers is examined and correlated with the graded glass transition behavior. The shape recovery response of the gradient SMP under a condition of continuous heating is demonstrated. This new class of SMP offers great potential for such applications as passive temperature sensing and precise control of shape evolution during a thermally triggered shape recovery. The figure below shows a functionally graded SMP being thermally triggered with uniform heating of the sample, leading to wave-like motion of the sample's edge. This new technology will allow engineers to design complex actuation schemes.

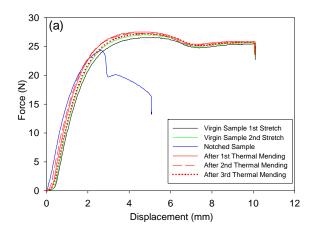


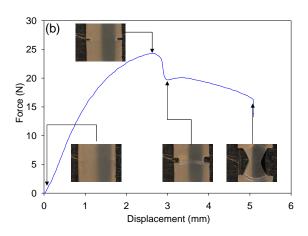
IV(iii) Development of a Shape Memory Assisted Self-Healing Polymer

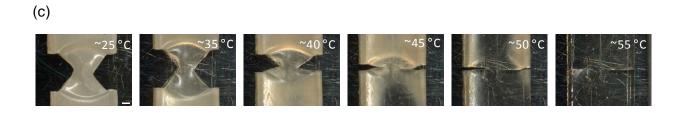
Erika D. Rodriguez, X. Luo, and P.T. Mather, "Linear and Crosslinked Poly (ε-Caprolactone) Polymers for Shape Memory Assisted Self-Healing (SMASH)," *ACS Applied Materials and Interfaces* **3** 152-161 (2011).

Self-healing (SH) polymers are responsive polymeric materials that can repair mechanical damage such as cracks in an autonomous fashion. In most SH polymers studies reported to date, crack closure was either unaddressed or achieved by manual intervention. Here, we developed a new strategy that utilizes shape memory (SM) to prepare novel SH polymers that are capable of simultaneously closing and re-bonding cracks with a simple thermal trigger. This strategy, termed "shape memory assisted self-healing (SMASH)" was demonstrated in a blend system consisting of crosslinked poly(ε-caprolactone) network (n-PCL) with linear poly(εcaprolactone) (I-PCL) interpenetrating the network, and which exhibits a combination of SM response from the network component and SH capacity from the linear component. Thermomechanical analysis revealed that the thermoset, n-PCL, demonstrates reversible plasticity – a form of shape memory where large plastic deformation at room temperature is fully recoverable upon heating. This SM action assists to close any cracks formed during deformation and/or damage while l-PCL chains tackify the crack surfaces by diffusion to the free surface and ultimately across the area of damage during the same heating step as used for SM. In our study, we investigated the controlled damage and SMASH healing of blends with varying composition using tensile testing of essential work of fracture film specimens. The healing component, l-PCL

used had a high  $M_w$  ( $M_w \sim 65 k$  g/mol) to enable re-entanglement after diffusion across the interface while the shape memory component, n-PCL was prepared from PCL telechelic diacrylates and a tetrathiol crosslinker, yielding excellent shape memory. We found excellent self-healing of films by the SMASH mechanism, with near complete healing for l-PCL contents exceeding 25wt-%. Applications are envisioned in the area of self-healing bladders, inflated structure membranes, and architectural building envelopes.







(a) Force vs. displacement curves for the virgin, damaged and healed state of a 1-PCL $_{50}$ :n-PCL $_{50}$  sample. (b) Notched 1-PCL $_{50}$ :n-PCL $_{50}$  sample showing stereo micrographs of deformation and crack growth clamped in the Linkam tensile stage. (Scale bar: 500  $\mu$ m) (c) Snapshots of crack closure and crack rebonding when the sample was unclamped from the Linkam tensile stage and heated to the temperatures shown above (stereo micrographs scale bar: 500  $\mu$ m).

# IV(iv) Modeling and Validation of Multi-Shape Memory Effects

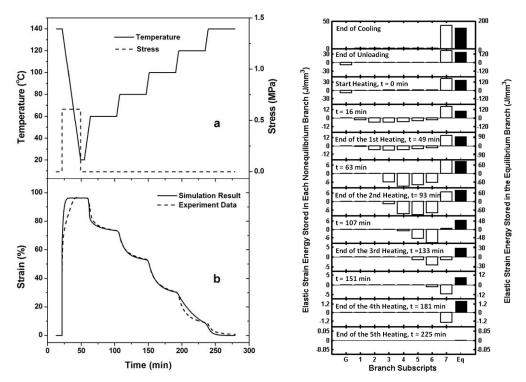
Our collaboration enabled interdisciplinary research involving both modeling and experiments to reveal mechanisms underlying mechanisms associated with multi-shape memory in materials developed in the Mather lab and in the Xie lab. Our findings have been published in two papers described below.

Ge, Q., Luo, X., Iversen, C.B., Mather, P., Dunn, M., Qi, H.J., 2012. Mechanisms of Triple-Shape Polymeric Composites Featuring Dual Thermal Transitions, *Soft Matter*, accepted.

Yu, K., Tao Xie, T., Leng, J., Ding, Y., Qi, H.J., 2012. Mechanisms of Multi-Shape Memory Effects and Associated Energy Release in Shape Memory Polymers, *Soft Matter*, v8, 5687 - 5695.

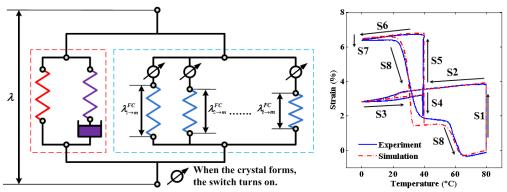
Multi-shape shape memory polymers have attracted significant research attention in recent years as the multiple shape change during a shape memory can greatly enhance the functionality of the polymers and their applications. To date, there are two methods to achieve m-SME. The first approach relies on a wide temperature of thermomechanical transition and the second mechanism uses distinguished thermal mechanical transitions. This work investigated mechanisms and developed thermomechanical models for m-SMPs based on these two mechanisms.

For m-SMPs based on a broad temperature range of thermomechanical transitions, we developed a multi-branch model, which is similar to the generalized standard linear solid model in viscoelasticity. In this model, individual nonequilibrium branches represent different relaxation modes of polymer chains with different relaxation times. As the temperature was increased in a staged manner, for a given temperature, different numbers of branches (or relaxation modes) became shape memory active or inactive, leading to the observed m-SME. For energy release during free recovery, under a tensile deformation of the SMP, stored energy in individual nonequilibrium branches was first transferred into a compressive deformation energy then gradually declined to zeros. Energy release during recovery was a complicated process due to the involvement of multiple relaxation modes.



(Left) Multi-SME simulated under stress controlled programming and staged heating recovery conditions.  $T_{r1}$  = 60 °C,  $T_{r2}$  = 80 °C,  $T_{r3}$  = 100 °C,  $T_{r4}$  = 120 °C,  $T_{r5}$  = 140 °C. **a,** temperature and stress history. **b,** strain evolution in both simulation and experiment. (Right) Elastic strain energy stored in each rubbery branch during the free recovery process of the multi-SME simulation.

For m-SMP based on distinguished thermomechanical transitions, we investigated the triple-shape polymeric composites (TSPCs). This composite is composed of an epoxy matrix, providing a rubber-glass transition to fix one temporary shape, and an interpenetrating crystallizable PCL (poly(ε-caprolactone)) fiber network providing the system the melt-crystal transition to fix a second temporary shape. A one-dimension (1D) model that combines viscoelasticity for amorphous shape memory polymers (the matrix) with a constitutive model for crystallizable shape memory polymers (the fiber network) is developed to describe t-SME. The model includes the WLF and Arrhenius equations to describe the glassy transition of the matrix, the kinetics of crystallization and the melting of the fiber network. An assumption that the newly formed crystalline phase of the fiber network is initially in stress-free state is used to model the mechanics of evolving crystallizable phases. Experiments to measure parameters including uniaxial tension, stress relaxation, and triple-shape memory testing were conducted. These parameters were then used to predict the t-SME in TSPC and showed excellent agreements with experiments.



(Left) Schematic of overall model: the total Cauchy stress consists of stresses on the matrix (red dashed box, left) and stress on fiber network (blue dashed box, right). (Right) Comparison between the model prediction and the experiment.

IV(v) Fabrication and Modeling of Two-Way Shape Memory Actuator

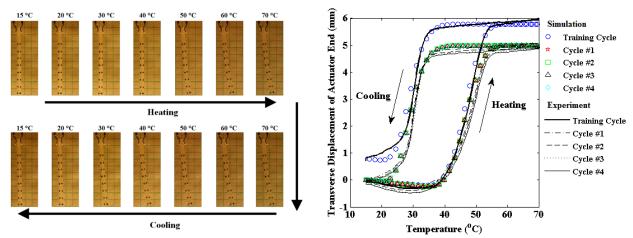
A principal goal of this AFOSR Project was to develope technology exploiting reversible shape memory actuation. Here, we pursued experiment and modeling for bimorph actuators incorporating a reversible SMP and an elastomer. This has resulted in two papers.

Kristofer K. Westbrook, Patrick T. Mather, Vikas Parakh, Martin L. Dunn, Qi Ge, Brendan M. Lee, H. Jerry Qi, 2011, Two-Way Reversible Shape Memory Effects in a Free-Standing Polymer Composite, *Smart Material and Structures*, 20, 065010 (9 pages).

Ge, Q., Westbrook, K.K., Mather, P.T., Dunn, M.L., Qi, H.J., Thermomechanical Behaviors of a Two-Way Shape Memory Composite Actuator, submitted.

Most SMPs exhibit a one-way shape memory (1W-SM) effect since one programming step can only yield one shape memory cycle; an additional shape memory cycle requires an extra programming step. Recently, a novel SMP that demonstrates both 1W-SM and two-way shape memory (2W-SM) effects was demonstrated by one of the authors (Mather). However, to achieve two-way actuation this SMP relies on a constant externally applied load. In this paper, an SMP composite where a pre-stretched 2W-SMP is embedded in an elastomeric matrix is developed. This composite demonstrates two-way shape memory effects in response to changes in temperature without the requirement of a constant external load. The transversal actuation of ~10% of actuator length is achieved. Cyclic tests show that the transversal actuation stabilizes after an initial training cycle and shows no significant decreases after 4 cycles. Furthermore, a theoretical model for the 2W-SMP based composite actuator was developed to investigate its thermomechanical behaviors and the mechanisms for the observed phenomena during the

actuation cycles, and to provide insight into how to improve designs.



(Left) An actuation during a heating-cooling cycle showing the free-standing 2W-SM effect; (Right) Predictions for the heating-cooling actuation cycles.

IV(vi) Thermomechanical Modeling of Shape Memory Polymers

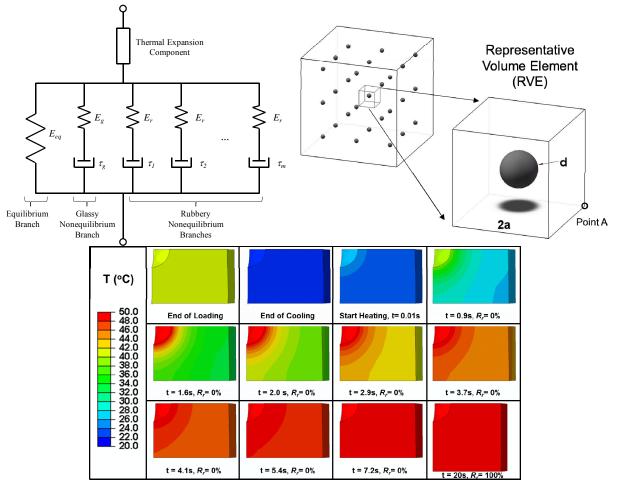
Westbrook, K.K., Kao, P.H., Castro, F., Ding, Y., Qi,H.J., 2011. A 3D Finite Deformation Constitutive Model for Amorphous Shape Memory Polymers: A Multi-Branch Modeling Approach for Nonequilibrium Relaxation Processes. *Mechanics of Materials*, v43: 853-869.

Ge, Q., Yu, K., Ding, Y., Qi, H.J., 2012. Prediction of Temperature Dependent Free Recovery Behaviors of Shape Memory Polymers, *Soft Matter*, 8, 11098–11105.

Yu, K., Westbrook, K.K., Kao, P.H., Leng, J., Qi, H.J., 2012. Design Considerations for Shape Memory Polymer Composites with Magnetic Particles, *J. Comp. Mat.*, accepted.

Shape memory polymers (SMPs) are materials that can recover a large pre-deformed shape in response to environmental stimuli. For a thermally activated amorphous SMP, the pre-deformation and recovery of the shape require the SMP to traverse its glass transition temperature ( $T_g$ ) to complete the shape memory (SM) cycle. As a result, the recovery behavior of SMPs shows strong dependency on both the pre-deforming temperature and recovery temperature. In these works, a multi-branch model is developed to capture the SM effect by considering the complex thermomechanical properties of amorphous SMPs as the temperature crosses  $T_g$ . The model utilizes two sets of nonequilibrium branches to capture two fundamentally different modes of relaxation: the glassy mode and Rouse modes. This leads to a significant reduction in the number of material parameters. Model simulation comparisons with a range of thermomechanical experiments conducted on a *tert*-butyl acrylate-based SMP show very good agreement. The model is further utilized to explore the intrinsic recovery behavior of an SMP

and the size effects on the free recovery characteristics of a magneto-sensitive SMP composite.



(Top Left) 1D rheological representation of the proposed model. (Top Right) The 3D representative volume element (RVE) for a magnetic particles reinforced SMP composite. (Bottom) Temperature distribution within the 3D RVE during the finite element analysis.

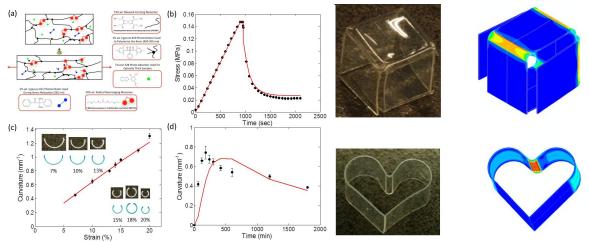
IV(vii) Photomechanical Modeling of Light Activated Polymers

Jennie Ryu, J., D'Ameto, M., Cui, X., Long, K.N., Qi, H.J., Dunn, M.L., 2012. Photo-Origami, *Applied Physics Letter*, 100, 161908.

*Photo-origami* uses the dynamic control of the molecular architecture of a polymer by a combination of mechanical and non-contact optical stimuli to design and program spatially- and temporally-variable *mechanical and optical fields* into a material. These fields are designed to enable controllable, sequenced, macroscopic bending and folding to create three-dimensional material structures that can additionally be functionalized and endowed with myriad properties;

examples include photonic and phononic metamaterials as well as biological tissue engineering constructs. The fields are essentially actuators, embedded in the material at molecular resolution. Here we demonstrate, through a combination of theory, simulation-based design, synthesis, and experiment, the operative phenomena and capabilities of photo-origami that highlight its potential as a powerful, and potentially manufacturable, approach to create three-dimensional material structures at macro, and even micro and nanometer scales. Although it is easy to conceptually realize objects via photo-origami, its ultimate impact lies in the fact that design can be guided by high-fidelity computational simulations based on a recently-developed theory that couples the hereditary nature of photophysics, chemistry, and large-deformation mechanics.

This work is the Feature Story for May 10, 2012 at phys.org (<a href="http://phys.org/news/2012-05-origami.html">http://phys.org/news/2012-05-origami.html</a>. It is also featured as one of the APL's 50th Anniversary Collection: Editor's Picks of Most Recent Publications.



(Left) a) Molecular constituents and mechanism of photo-induced stress relaxation; Measured (red symbols) and simulated (black lines) photomechanical behavior that serves as the foundation for photo-origami: b) photoactivated stress relaxation; c) curvature vs. applied strain for uniformy-irradiated strips with actual and simulated deformed shapes shown in the inset; d) curvature vs. time at a prescribed strain. (Right) A box and a heart fabricated by photo-origami.

# V. Personnel Supported

a. Number of PI's and Co-PI's involved in the research project: 3

PI: Prof. Patrick T. Mather co-PI: Prof. Jerry Qi

### co-PI: Prof. Martin Dunn

- **b.** Number of Post Docs Supported in the last 12 months under AFOSR: **0**
- **c.** Number of graduate students supported in the last 12 months: the equivalent of **2** graduate assistants.
- d. Other researchers supported in the last 12 months by AFOSR: 6

Graduate students (partial support): Amir Torbati, Erika Rodriguez, Vikas Parakh, Qi Ge, Kai Yu, Jennie Ryu

Undergraduate students (partial support): Erika Brenner, Ellen Benn, Derek Weed, Sabrina Kowalski, Andrew DiOrio, Maria Mintskovsky.

### VI. Publications

Publications by PI submitted, accepted, or appearing in the last 12 months period in refereed journals and referencing AFOSR support: 3

Qi Ge, Xiaofan Luo, Erika D. Rodriguez, Xiao Zhang, Patrick T. Mather, Martin L. Dunn, H. Jerry Qi, "Thermo-mechanical Behaviors of Shape Memory Elastomer Composites," submitted to *Journal of Mechanics and Physics of Solids* (2011).

A.M. DiOrio, X. Luo, K.-M. Lee, and P.T. Mather, "A Functionally Graded Shape Memory Polymer," *Soft Matter* **7** 68-74 (2011).

Erika D. Rodriguez, X. Luo, and P.T. Mather, "Linear and Crosslinked Poly (ε-Caprolactone) Polymers for Shape Memory Assisted Self-Healing (SMASH)," *ACS Applied Materials and Interfaces* **3** 152-161 (2011).

Ge, Q., Luo, X., Iversen, C.B., Mather, P., Dunn, M., Qi, H.J., 2012. Mechanisms of Triple-Shape Polymeric Composites Featuring Dual Thermal Transitions, *Soft Matter*, accepted.

Ge, Q., Yu, K., Ding, Y., Qi, H.J., 2012. Prediction of Temperature Dependent Free Recovery Behaviors of Shape Memory Polymers, *Soft Matter*, 8, 11098–11105.

Jennie Ryu, J., D'Ameto, M., Cui, X., Long, K.N., Qi, H.J., Dunn, M.L., 2012. Photo-Origami, *Applied Physics Letter*, 100, 161908. (Feature Story for May 10, 2012 at phys.org (http://phys.org/news/2012-05-origami.html)

Yu, K., Westbrook, K.K., Kao, P.H., Leng, J., Qi, H.J., 2012. Design Considerations for Shape Memory Polymer Composites with Magnetic Particles, *J. Comp. Mat.*, accepted.

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Kristofer K. Westbrook, Patrick T. Mather, Vikas Parakh, Martin L. Dunn, Qi Ge, Brendan M. Lee, H. Jerry Qi, 2011, Two-Way Reversible Shape Memory Effects in a Free-Standing Polymer Composite, *Smart Material and Structures*, 20, 065010 (9 pages).

Ge, Q., Westbrook, K.K., Mather, P.T., Dunn, M.L., Qi, H.J., Thermomechanical Behaviors of a Two-Way Shape Memory Composite Actuator, submitted.

### VII. Interactions and Transitions

a. Participation and Presentations at Meetings

### Invited Lectures (33)

- H. Jerry Qi, Physics and Mechanics of Shape Memory Polymers, Hong Kong PolyTechnic University, July 28, 2010.
- P.T. Mather, X. Luo E.D. Rodriguez, and D.C. Weed, "Laminated Shape Memory Elastomeric Composites," 4th International Conference on Smart Materials, Structures, and Systems, Session A15: Actively Moving Polymers, Montecatini Terme, ITALY, June 10-14, 2012.
- P.T. Mather, "Advances in methods of making shape memory polymers for biomedical applications," Xianhshan Science Conference, Beijing, CHINA, May 29-30, 2012.
- I.U. Onyejekwe, X. Luo, and <u>P.T. Mather</u>, 2012 Biotechnology Symposium, Drug Delivery/Nanotechnology Session, "Drug Delivery from Shape Memory Elastomeric Composites," Syracuse, NY, May 21, 2012.
- P.T. Mather, Temple University, Bioengineering Program, "Shape Memory Polymers: A World of Opportunities in Healthcare," Philadelphia, PA, May 4, 2012.
- P.T. Mather, TA Instruments Users Meeting and Symposium, "Analysis of Shape Memory Polymers," New Orleans, LA, April 29-May 2, 2012.
- I.U. Onyejekwe, X. Luo, and <u>P.T. Mather</u>, SPE ANTEC, New Technology Forum on Polymer Applications in Health, "Drug Delivery from Shape Memory Elastomeric Composites," Orlando, FL, April 3, 2012.

- P.T. Mather, CUNY Staten Island, Department of Chemistry, "Bulk and Surface Shape Memory in Polymers," Staten Island, NY, March 21, 2012.
- P.T. Mather, Merial Corporation, "Innovations in Shape Memory Polymers for Drug Delivery," 3/12/2012.
- P.T. Mather, American Physical Society, March Meeting, "Surface Shape Memory in Polymers," in the Session on "Inherently Strained Polymers and Soft Materials", Boston, MA, February 27, 2012
- P.T. Mather, Drexel University, Department of Chemical and Biological Engineering, "Surface Shape Memory in Polymers," January 18, 2012; Philadelphia, PA.
- P.T. Mather, Aerospace Applications of Polymers, 242nd ACS National Meeting and Exposition, "Epoxy-Based Liquid Crystalline Epoxies," August 28, 2011, Denver, CO.
- P.T. Mather, Syracuse Rotary, "Smart Polymers at Syracuse Biomaterials Institute," August 19, 2011.
- P.T. Mather, 2nd International Conference on Nanotechnology: Fundamentals and Applications, "Soft Shape Memory Nanocomposites: From Self-Assembly to Electrospinning," Ottawa, ON, CANADA; July 27-29, 2011.
- P.T. Mather, American Chemical Society, Syracuse Section, "Nanoscale Polymeric Biomaterials," (colecture with Rebecca A. Bader) Syracuse University, Syracuse, NY, July 14, 2011.
- P.T. Mather, Avon Products, Inc., "Innovations in Shape Memory Polymers," and "Smart Polymers@Syracuse," Suffern, NY, July 13, 2011.
- P.T. Mather, MD&M East (Medical Device & Engineering East Exposition), w/ J.M. Hasenwinkel, M.M. Maye, and J.L. Gilbert, "Biomaterials Innovations at Syracuse University," New York, NY, June 8, 2011.
- P.T. Mather, Institute for Advanced Materials, University of North Carolina, Chapel Hill, Leaders in Materials Science Series (inaugural event), "Innovations in Shape Memory Polymers," Chapel Hill, NC, April 15, 2011.
- P.T. Mather, Liquid Crystal Institute, Kent State University, "Shape Memory Polymers," Kent, OH, March 16, 2011.
- P.T. Mather, Chemical Engineering Department, McGill University, "Shape Memory Polymer Nanocomposites: From Smectic Self-Assembly to Electrospinning," Montreal, Quebec, CANADA, January 10, 2011.
- P.T. Mather, Materials Research Society, Fall Meeting, Symposium L: Liquid Crystal Materials: Beyond Displays, "Shape Memory Liquid Crystalline Elastomers," Boston, MA, November 29, 2010. Coauthors: Kelly A. Burke, Xiaofan Luo, Amir H. Torbati, Ellen E. Benn.
- P.T. Mather, Boston Scientific Corporation, "Functional Polymer Innovations: Shape Memory, Self-Healing, and Antimicrobial Materials," Maple Grove, MN, November 2, 2010.
- P.T. Mather, Biomedical Engineering Department, University of Florida, "Biodegradable Shape Memory

- Polymers," Gainesville, FL, October 1, 2010.
- P.T. Mather, US-Japan Workshop on Reconfigurable Multifunctional Systems, "Shape Memory Polymer Nanocomposites: from Smectic Self-Assembly to Electrospinning," Hokkaido University, Sapporo, JAPAN, Sept. 8-10, 2010.
- P.T. Mather, International Materials Research Congress XIX, P.T. Mather and Kelly A. Burke, "Main-Chain Liquid Crystalline Elastomers for Soft Shape Memory," August 17, 2010, Cancun, MEXICO.
- P.T. Mather, Instituto de Ciencias Fisicas, National Autonomous University of Mexico (UNAM) "Electrospun Smart Polymeric Composites," August 13, 2010, Cuernavaca, MEXICO.
- P.T. Mather, Baxter Healthcare, "Functional Polymer Innovations: Shape Memory, Self-Healing, and Antimicrobial Materials," June 23, 2010, Chicago, IL.
- P.T. Mather, ACS Regional Meeting, CeRMACS, "Electrospun Smart Polymeric Composites," Dayton, Ohio, June 18, 2010. (with X. Luo and E.D. Rodriguez)
- P.T. Mather, WE-Heraeus-Seminar on Biodegradable Polymers as Biomaterials, "Biodegradable Shape Memory Nanocomposites," Bad Honnef, GERMANY, May 31, 2010.
- P.T. Mather, Society of Plastics Engineering ANTEC 2010, Polymer Analysis Division, Keynote Lecturer, "Nanofiber-Based Shape Memory Composites," May 18, 2010. Orlando, FL.
- P.T. Mather, Dept. of Polymer Engineering, University of Akron, "Nanofiber-Based Polymeric Composites," April 2, 2010.
- P.T. Mather, 3<sup>rd</sup> Indo-American Frontiers of Engineering (IAFOE), Agra, India, "Smart Polymers: from Shape Memory to Self-Healing," March 12, 2010.
- Qi, H.J. Multiphysical Behaviors of Shape Memory Polymers, Beijing Jiaotong University, Beijing, China, 12/2/2011.

### Contributed Talks (14)

- Qi, G., Dunn, M., Qi, H.J., Mather, P.T., "Constitutive Model of Shape Memory Elastomeric Composites (SMECs)", ASME 2010 IMECE, Vancouver, BC, CA, November 2010.
- Qi, H.J., Ge, Q., Dunn, M., Mather, P., "Constitutive Model of Shape Memory Elastomeric Composites (SMECs)", The 7th International Conference on MTDM, Portoroz, Slovenia, September, 2010
- B. Alvarado-Tenorio, A. Romo-Uribe, P.T. Mather, "Crystalline and Nanoscale Structure in Shape Memory Hybrid Nanocomposites Determined by Simultaneous WAXS-SAXS Analysis," Materials Research Society, Fall Meeting, Symposium HH: Polymer-Based Smart Materials, Boston, MA, November 29, 2010.
- Estefania Huitron-Rattinger, K. Ishida, A. Romo-Uribe, P.T. Mather, "Hybrid Polyurethane Nanocomposites: Synthesis and Microstructure," Materials Research Society, Fall Meeting, Symposium HH: Polymer-Based Smart Materials, Boston, MA, November 29, 2010.

- <u>K. Ishida</u>, Estefania Huitrón-Rattinger, Angel Romo-Uribe, Patrick T. Mather, "Synthesis and characterization of POSS-containing polyurethane cationomers," 82<sup>nd</sup> Annual Meeting of Society of Rheology, Santa Fe, NM October 27, 2010.
- Erika D. Rodriguez, Xiaofan Luo and Patrick T Mather. Systems of Linear and Crosslinked Poly (e-Caprolactone Polymers for Shape Memory Assisted Self-Healed (SMASH). Society for the Advancement of Material and Process Engineering (SAMPE) Conference. October, 2010.
- Kelly A. Burke, X. Luo, and P.T. Mather, "Characterization of new surface shape memory phenomena in soft and rigid shape memory polymers," 82<sup>nd</sup> Annual Meeting of Society of Rheology, Santa Fe, NM October 27, 2010.
- X. Gu and P.T. Mather, "Hardblock-free thermoplastic polyurethanes (TPUs) exhibiting shape memory," ACS National Meeting, Boston, MA, August 24, 2010.
- K.A. Burke and P.T. Mather, "Evolution of Microstructure During Strain Recovery of a Shape Memory Liquid Crystalline Elastomer," ACS National Meeting, Boston, MA, August 22, 2010.
- K.A. Burke and <u>P.T. Mather</u>, "Main-Chain Liquid Crystalline Elastomers as Shape Memory Polymers," ACS National Meeting, Boston, MA, August 23, 2010.
- P.T. Mather, Q. Guo, J. Wu, P.T. Knight, "Blends of Paclitaxel with POSS-based biodegradable polyurethanes," International Materials Research Congress XIX, Nanomaterials for Biomedical Applications Symposium, August 16, 2010. Cancun, MEXICO.
- Xiaofan Luo and <u>Patrick T. Mather</u>, "Design Principles of New Shape Memory Polymeric Composites," ACS NERM, Potsdam, NY, June 3, 2010.
- Richard Baker, Patrick T. Mather and James H. Henderson, "Composition Optimization of Transition Temperature and Breadth of Glassy Shape Memory Polymers," NERM, Potsdam, NY, June 3, 2010.
- Jian Wu, Xinzhu Gu and Patrick T. Mather\*, "Biostable Multiblock Thermoplastic Polyurethanes incorporating Poly(ε-caprolactone) and Polyhedral Oligomeric Silsesquioxane (POSS)" Society for Biomaterials Annual Meeting: Engineering Materials for Medical Use: The New, the improved and the Coated, Seattle, Washington, April 21-24, 2010.
- Qi Ge, Xiaofan Luo, Patrick Mather, Martin Dunn, H. Jerry Qi, Thermomechanical Constitutive Modeling of Shape Memory Elastomeric Composites, 2011 SEM conference, Uncasville, CT, June 13-16, 2011.
- Kristofer Westbrook, Qi Ge, H. Jerry Qi, Time-dependent Recovery of Shape Memory Polymers, SES 2011 Annual Conference, Evanston, IL, October, 12-14, 2011.
- Binglian Wang, Qi Ge, Kevin Long, H. Jerry Qi A General 3D Thermal-mechanical Constitutive Model for Soft Active Materials with Phase Evolution, 2011 IMECE, Denver, CO., Nov. 14-17, 2011.
- Qi Ge, Martin Dunn, H. Jerry Qi, Thermo-mechanical Behaviors of Shape Memory Elastomer Composites, 2011 IMECE, Denver, CO., Nov. 14-17, 2011.

# **b.** Consultation and Advisory Functions with other Laboratories and Agencies

This project is a close collaboration with Dr. Greg Reich of AFRL/RBSA on active materials for the DCT project. This has led to detailed designs that will incorporate our materials, as well as connections to Prof. Sharon Swartz (Brown University) and Shiv Josi (NexGen).

**c.** No transitions to practiced technology exist for this research as yet.

# **VIII.** New Discoveries, Inventions or Patent Disclosures.

One invention: "Mechanically Activated Shape Change"

Inventors: P.T. Mather and E.D. Rodriguez

Disclosure to be filed with Syracuse University Technology transfer office

# **IX.** Awards and Honors received by the PI (life-time received): 22

Invited Participant/Speaker in NAE Indo-American Frontiers of Engineering (IAFOE) Symposium					
Fellow, Society of Plastics Engineers					
Fellow, American Institute for Medical and Biological Engineering					
Case Western Reserve University, Finalist for Wittke Award for Undergraduate Teaching					
Case Western Reserve University, Undergraduate Student Government Teaching Excellence Award					
Keynote Lecturer Applied Rheology Special Interest Group (ARSIG)					
SPE ANTEC 2005					
Rogers Corporation Award for Outstanding Teacher in Chemical Engineering					
SPE Medical Plastics Division, ANTEC 2002 Best Paper Award					
Member of AFOSR Star Team, "Lightweight Low-Cost Membrane Structures"					
School of Engineering Outstanding Junior Faculty Award, University of Connecticut					
NSF CAREER Award, "Orientational Dynamics in Flows of Thermotropic Polymers" 200					
AFRL-Sponsored Assessment Team, "Applicability of Organic Matrix Composites					
to Cryogenic Rocket Propulsion applications," Sp	ring 2001				
Who's Who in Plastics and Polymers					
SPE Engineering Properties and Structure Division, <i>Best Paper</i> , 55 <sup>th</sup> ANTEC					
Member of AFOSR Star Team, "Inorganic Synthesis"					
USAF Palace Knight Fellowship 199					
National Defense Science and Engineering Grad. Fellowship (A.R.O.)					
University Scholars - Penn State Honors Curriculum 198					
Tau Beta Pi					
Best Summer Research, Rohm and Haas Company					

Golden Key National Honor Society George Gleeson Scholarship for Undergraduate Research 1989-present 1989-1990